



PATENT APPLICATION

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicants: Atsushi YABE et al

For: ELECTROLESS COPPER PLATING SOLUTION

Serial No.: 10/576 231 Group: 1792

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DECLARATION UNDER 37 CFR 1.132

I, the undersigned, hereby declare as follows:

I am one of the inventors of the invention described and claimed in application Serial No. 10/576 231, filed on April 14, 2006.

I hereby incorporate by reference thereto the contents of the Examples and Comparative Examples contained on pages 8-13 of application Serial No. 10/576 231.

I have performed additional tests to further illustrate the importance of the water-soluble nitrogen-containing polymer in the present invention.

Example 6 was performed in the identical manner as Example 2 in application Serial No. 10/576 231 except that polyethyleneimine was substituted for polyacrylamide in an identical amount in the electroless copper plating solution. The contents of the other ingredients were identical to that of Example 2.

In Example 7, polyvinylpyrrolidone was substituted for polyacrylamide of Example 2 in application Serial No.

10/576 231 in an identical amount with the contents of the remaining ingredients in the electroless copper plating solution being the same as Example 2.

Example 6

A silicon wafer with a tantalum nitride film was pretreated by the same method as in Example 1 of application Serial No. 10/576 231, after which the wafer was electroless plated with copper for 30 minutes at 60°C. The composition of the plating solution was copper sulfate 0.04 mol/L, ethylenediaminetetraacetate 0.4 mol/L, glyoxylic acid 0.1 mol/L, phosphinic acid 0.1 mol/L, 2,2'-bipyridyl 10 mg/L, and polyethyleneimine (Mw 10,000, Mw/Mn = 2.5) 5 mg/L, and the pH was 12.5 (pH regulator: potassium hydroxide). The plating film was formed uniformly without unevenness, and the film thickness was 100 nm. The mirror surface portion of the plating film was subjected to the tape peel test after the plating, which revealed good adhesion, with no peeling at all. Cleavage plane SEM observation revealed that the trench portions had been embedded with no voids. TEM observation for a cross-section after annealing revealed the crystal grain size of the trench portions to be small, at about 20 nm, which was the same as the size outside the trenches.

Example 7

A silicon wafer with a tantalum nitride film was pretreated by the same method as in Example 1 of application Serial No. 10/576 231, after which the wafer was electroless plated with copper for 30 minutes at 60°C. The composition of the plating solution was copper sulfate 0.04 mol/L, ethylenediaminetetraacetate 0.4 mol/L, glyoxylic acid 0.1 mol/L, phosphinic acid 0.1 mol/L, 2,2'-bipyridyl 10 mg/L, and polyvinylpyrrolidone (Mw 40,000, Mw/Mn = 2.7) 5 mg/L, and the pH was 12.5 (pH regulator: potassium hydroxide). The plating film was formed uniformly without unevenness, and the film thickness was 120 nm. The mirror surface portion of the

plating film was subjected to the tape peel test after the plating, which revealed good adhesion, with no peeling at all. Cleavage plane SEM observation revealed that the trench portions had been embedded with no voids. TEM observation for a cross-section after annealing revealed the crystal grain size of the trench portions to be small, at about 20 nm, which was the same as the size outside the trenches.

Example 8

A silicon wafer having a trench pattern with an aspect ratio of 2 and a line width of 150 nm, on which a film of ruthenium had been formed in a thickness of 10 nm by sputtering, was prepared.

The silicon wafer with the ruthenium film was electroless plated with copper for 40 minutes at 60°C. The composition of the plating solution was copper sulfate 0.02 mol/L, ethylenediaminetetraacetate 0.08 mol/L, glyoxylic acid 0.12 mol/L, phosphinic acid 0.09 mol/L, and polyacrylamide (Mw 1,000,000, Mw/Mn = 1.5) 10 mg/L, and the pH was 12 (pH regulator: tetramethylammonium).

The plating film was formed uniformly without unevenness, and the film thickness was 80 nm. The mirror surface portion of the plating film was subjected to the tape peel test after the plating, which revealed good adhesion, with no peeling at all. Cleavage plane SEM observation revealed that the trench portions had been embedded with no voids. TEM observation for a cross-section after annealing revealed the crystal grain size of the trench portions to be at least 100 nm, which was far larger than the about 20 nm size outside the trenches.

DISCUSSION OF RESULTS

Examples 6 and 7 presented above show that while polyethyleneimine and polyacrylamide can both be used in the electroless copper plating solution of the present invention and produce excellent results, the water-soluble nitrogen-containing polymer of the present invention is not limited to

just polyethyleneimine and polyacrylamide. Example 7 uses polyvinylpyrrolidone as the water-soluble nitrogen-containing polymer and likewise produces excellent results.

Example 8 illustrates that the electroless copper plating solution can be applied to substrates other than a silicon wafer having a tantalum nitride film and still produce excellent results. In Example 8, a substrate made of silicon with a ruthenium film was electrolessly plated with an electroless copper plating solution according to the present invention and a superior plating result was obtained.

I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: April 8, 2009

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